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Test of variational transition state theory with multidimensional tunneling contributions against experimental kinetic isotope effects for the CH_nD_{4-n} + $OH \rightarrow P$ (n = 0, 4) reactions

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Abstract. Variational transition state theory including tunneling corrections (as implemented in Polyrate 8.7) and using multilevel energy calculations at the MCCM-CCSD(T)-1sc level for the CH_4 + OH reaction and at the MCCM-CCSD(T)-2m level for the CD_4 + OH process, reproduces very well the experimental rate constants. However, no single methodology was found that reproduces equally well the experimental rate constants for both title reactions.

Key words: Kinetic isotope effects – Multicoefficient correlation methods – Variational transition state theory rate constants – Reoriented dividing surface algorithm – CH_4 + OH reaction

The rate constants for the reaction of OH with methane and for several of its H/D isotopic variants have been the object of several experimental measurements [1] and theoretical calculations in the past [2]. The reactions of OH with methane and partially halogenated alkanes are especially important for controlling the balance of species in the upper atmosphere. In addition, the theoretical computation of accurate rate constants for the reaction of OH with methane and each of its deutero-isotopomers, has been, and still is, a challenge for electronic structure methods and dynamical approaches. One dynamical scheme that has been widely tested [3] against benchmark rate constants is variational transition state theory with multidimensional tunneling contributions (VTST/MT) [4]. However, the VTST/MT rate constants published in the literature for the title reactions, obtained with different levels of electronic structure calculations, do not match exactly the available experimental rate constants even though the results were quite good from a quantitative point of view (Melissas and Truhlar (1993), Hu et al. (1994), Espinosa-García and Corchado (2000), and Masgrau et al. (2001) [2]). In the last of these papers, we carried out a test of variational transition state theory plus multidimensional tunneling corrections using different multilevel electronic approaches. In particular, we used several of the MCSAC (multicoefficient scaling all correlation energy) and the MCCM (multicoefficient correlation methods) [5]. The so-called MCCM-CCSD(T)-1sc multilevel scheme provided the rate constants most comparable with the experimental ones for the reactions of OH with CH_4 and CD_4. Those results were good enough for most practical applications in the whole range of temperatures studied (especially for the perprotio reaction), although the deviation from experiment was larger at lower temperatures. Interestingly, the kinetic isotope effects (KIEs) were not so well reproduced because the deviations from the experimental values of the individual theoretical rate constants of the two different isotopologs, although being very small, are in opposite directions. The version of VTST/MT that we tested was CVT/SCT, in which CVT [6] stands for canonical variational theory and SCT [7] means the small curvature tunneling approximation. The MCCM-CCSD(T)-1sc multilevel electronic energy calculations mentioned above were used within a dual-level direct dynamics scheme known as the interpolated single-point energy correction (ISPE) [8]. This dual-level direct dynamics approach consisted in calculating a low-level MP2(full)/cc-pVTZ minimum energy path (MEP), with scaled generalized-normal-mode vibrational frequencies (with a scale factor of 0.9790) computed at the same level for selected points along this path. Then, multilevel single-point classical energy calculations were carried out at the stationary points and at several non-stationary points along the MEP as the high-level electronic information to correct the energetics. In addition, the reoriented dividing surface (RODS) algorithm [9] was applied to improve the generalized-normal-mode frequencies along the low-level MEP. Those calculations were carried out with POLYRATE version 8.5.1 [10].

Very recently, an improved version of the code was released. In particular, the modification affects the reaction path curvature vector calculation in the SCT

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methodology when the RODS algorithm is used. The question arises of whether that change could ameliorate the description of the KIEs. So, in this letter the KIEs corresponding to the reactions: CH_4/CD_4 + OH → H_2O/HDO + CH_3/CD_3 have been computed again with the improved RODS and SCT algorithms in POLYRATE 8.7 [11]. The three multilevel methods that will be tested are the MCCM-CCSD(T)-1sc, the MCCM-CCSD(T)-2sc and the MCCM-CCSD(T)-2m, and the dual-level direct dynamics approach will be the same as in our previous paper (last Ref. in [2]). The notation 1sc, 2sc, and 2m refers to the way in which the core-correlation and spin-orbit contributions are introduced and to the molecular data set used in the parametrization of the method.

In Fig. 1a the CVT/SCT rate constants for the CH_4 + OH reaction obtained with each one of the three selected direct dynamics methodologies are plotted, along with the experimental values, with respect to temperature. All the theoretical rate constants are improved in comparison with our previous calculations (last Ref. in [2]), especially in the lowest temperature range where tunneling is most significant, and where the improvement in the SCT algorithm in the new version of the code is expected to be more relevant. In the new calculations, the dynamical approach that gives the smallest average absolute deviation (19%) between the CVT/SCT rate constants and the experimental values, over the whole analyzed temperature range, is again the direct dynamics methodology based on the classical energy calculation at the MCCM-CCSD(T)-1sc level (note that the deviation is only of 3% between 298 °K and 420 °K). The CVT/SCT rate constants at the MCCM-CCSD(T)-2sc level are only slightly smaller (mean absolute deviation of 23%) although their behavior is better at the two lowest temperatures. These deviations are comparable to the average absolute deviation of 25% attributed to the intrinsic error of variational transition state theory with optimized multidimensional tunneling contributions (VTST/OMT) by a recent systematic comparison (by Allison and Truhlar [3]) of harmonic VTST/μOMT to 231 benchmark rate constants for colinear and three-dimensional atom-diatom reactions. At the MCCM-CCSD(T)-2m level the CVT/SCT rate constants slightly underestimate the experimental results and show greater deviations from experiment than the other two dynamical calculations. In Fig. 1b the rate constants calculated for the CD_4 + OH reaction with the three multilevel approaches are plotted along with experimental values as a function of temperature. The dynamical methodology based on corrected energies at the MCCM-CCSD(T)-2m level shows now a very small absolute average deviation, of only 10% from 298 °K to 700 °K, for this isotope variant of the perprotio reaction. However, the two other dynamical approaches based on multilevel classical energies at the MCCM-CCSD(T)-1sc and the MCCM-CCSD(T)-2sc levels overestimate the experimental rate constants, especially in the lowest temperature range, in contrast to the high accuracy attained for the CH_4 + OH reaction. In summary, none of these three dynamical approximations presents the same accuracy in the calculation of the rate constants for the CH_4 + OH and the

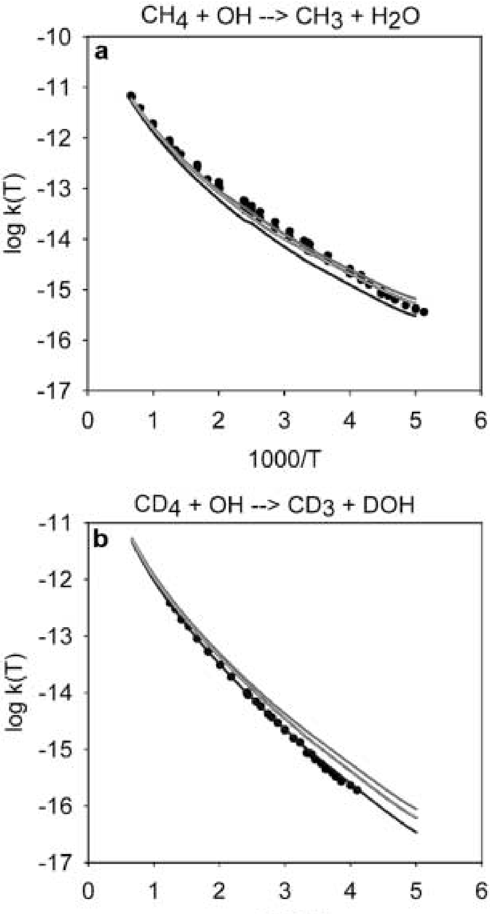

Fig. 1a, b. Arrhenius plots for the experimental and calculated rate constants of the reactions: **a** $CH_4 + OH \rightarrow CH_3 + H_2O$; **b** $CD_4 + OH \rightarrow CD_3 + DOH$. Rate constants are in cm^3 $molecule^{-1}$ s^{-1} and temperatures in Kelvin. Experimental data from Ref. [1] (*circles*); MCCM-CCSD(T)-1sc (*red*); MCCM-CCSD(T)-2sc (*green*); MCCM-CCSD(T)-2m (*blue*)

Table 1. Experimental and calculated KIEs at several temperatures for the reactions: $CH_4/CD_4 + OH \rightarrow CH_3/CD_3 + H_2O/DOH$

T(K)	1sc[a]	1sc[b]	2m[c]	2sc[d]	Exp[e]
200	3.66	7.45	8.85	8.58	
223	3.14	5.65	6.47	6.41	
298	2.38	3.30	3.57	3.65	7.36
300	2.36	3.27	3.68	3.61	
365	2.16	2.69	2.82	2.54	4.94
409	2.04	2.43	2.52	2.26	4.04
416	2.02	2.39	2.49	2.21	3.99
498	1.65	1.85	1.91	1.91	3.30
602	1.53	1.64	1.68	1.70	2.63
704	1.44	1.52	1.55	1.55	2.31
1000	1.30	1.34	1.34	1.37	
1500	1.12	1.13	1.14	1.16	

[a] MCCM-CCSD(T)-1sc (POLYRATE 8.5.1). [b] MCCM-CCSD(T)-1sc (POLYRATE 8.7). [c] MCCM-CCSD(T)-2sc (POLYRATE 8.7). [d] MCCM-CCSD(T)-2m (POLYRATE 8.7).
[e] From Ref. [1].

CD_4 + OH reaction, that is, we have not found a unique methodology that reproduces equally well the experimental rate constants for both title reactions.

In Table 1 the calculated KIEs at all the temperatures analyzed are compared to the experimental values at some particular temperatures. With the improved version of the code the calculated KIEs increase by a factor of 2.04 at 200 °K to a factor of 1.03 at 1000 °K (compare columns two and three of Table 1). Nevertheless, the theoretical KIEs calculated with the three different dynamical methodologies still underestimate the experimental results at all the temperatures. This underestimation in the calculated KIEs with the theoretical approaches that use corrected energies at the MCCM-CCSD(T)-1sc and the MCCM-CCSD(T)-2sc levels comes from the somewhat high values obtained for the deutero-isotopomer rate constants. In contrast, the MCCM-CCSD(T)-2m KIEs are small because the rate constants for the perprotio reaction are underestimated. Therefore, although we have achieved a significant improvement of the calculated KIEs of the title reaction, especially at low temperatures, it is clear that additional theoretical work is still needed to ameliorate them.

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